PRODUCTS OF FRIEDEL-CRAFTS ACYLATION OF AMINONAPHTHALENES AS POSSIBLE PRECURSORS OF BENZOCINNOLINES

BY

ARCHIBALD MILLER HYSON

B.S., Pennsylvania State College, 1942
M.S., University of Illinois, 1944

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY
IN THE GRADUATE COLLEGE OF THE
UNIVERSITY OF ILLINOIS, 1949

URBANA, ILLINOIS

1949

PRODUCTS OF FRIEDEL-CRAFTS ACYLATION OF AMINONAPHTHALENES AS POSSIBLE PRECURSORS OF BENZOCINNOLINES

BY

ARCHIBALD MILLER HYSON

B.S., Pennsylvania State College, 1942
M.S., University of Illinois, 1944

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY
IN THE GRADUATE COLLEGE OF THE
UNIVERSITY OF ILLINOIS, 1949

URBANA, ILLINOIS

1949

ACKNOWLEDGMENT

The author wishes to express his gratitude to Dr. Nelson J. Leonard for proposing this investigation and for his guidance and encouragement during its course.

PRODUCTS OF FRIEDEL-CRAFTS ACYLATION OF AMINONAPHTHALENES AS POSSIBLE PRECURSORS OF BENZOCINNOLINES

Introduction

The diazotization and subsequent cyclization of *ortho*-aminoaryl alkyl ketones is of such generality (1,2,3) as to serve as a positive indication of the vicinal arrangement of the amino and acyl groups on the aromatic nucleus in such compounds. When it was discovered (4) that the compound reported (5) to have the structure 2-amino-1-acetonaphthone did not form a hydroxycinnoline under the usual diazotization and cyclization conditions, there was reasonable doubt as to the validity of the assigned structure of the amino-acetonaphthone. Therefore, this compound was subjected to degradative study to determine the position at which the acetyl group had entered the molecule.

In general, the application of the Friedel-Crafts reaction to the acylation of aminonaphthalenes has been somewhat limited. Hence, it was also of interest to study the Friedel-Crafts acetylation of 1-naphthylamine and of the naphthalene-diamines in order to learn more about orientation effects in the naphthalene nucleus. Any of the products possessing a vicinal amino and acetyl group would serve as intermediates in the preparation of hydroxybenzocinnolines.

Discussion Of Results

The structure of the predominant product of Friedel-Crafts acetylation of acet-2-naphthalide has been proved to be 7-amino-1-acetonaphthone. It has also been shown that a smaller amount of 6-amino-2-acetonaphthone was formed simultaneously. Similar results were obtained with 2-naphthylamine. By a critical evaluation of the literature in combination with the results of this investigation, the product

of analogous acetylation of 2-bromo- or 2-chloronaphthalene has been shown to be mainly the corresponding 7-halo-1-acetonaphthone instead of the 2-halo-1-acetonaphthone as previously reported (6).

These conclusions have made necessary the revision of the structures of numerous related naphthalene derivatives described in the literature as 1,2-substituted compounds.

The Friedel-Crafts acetylation of acet-1-naphthalide or of 1-naphthylamine gave 4-amino-1-acetonaphthone as the principal product together with a smaller quantity of 5-amino-1-acetonaphthone.

After having separately determined the orientating effects of an *alpha*- and *beta*-amino or acetylamino group in the naphthalene nucleus, the effects of two such groups were studied. Eight of the ten possible naphthalenediamines were prepared and were subjected to Friedel-Crafts acetylation, either as the free amine or as the diacetyl derivative. Six of these compounds — 1,2-naphthalenediamine, 1,4-naphthalenediamine, 1,5-naphthalenediamine, 2,6-naphthalenediamine, 2,7-naphthalenediamine and 1,8-naphthalenediamine — failed to undergo ring acylation. The 1,6- and 1,7-naphthalenediamines underwent substitution exclusively in the 4-position to give 4,7-diamino-1-acetonaphthone and 4,6-diamino-1-acetonaphthone, respectively. The 1,3- and 2,3-naphthalenediamines were not subjected to Friedel-Crafts acetylation.

In general, the Friedel-Crafts acylation reaction with the naphthalenediamines fails if the activated positions are *ortho* or *peri* to an amine residue.

The observed orientation in the naphthalene nucleus containing amino or acetylamino groups is undoubtedly caused by two factors: (1) polarization effects created by the presence of the electronegative group on the nucleus, (2) steric influences. The normal activating influence of the amino group is probably modified by complex formation with an aluminum chloride molecule. This phenomenon would also increase the

effective size of the amino group, thus enhancing the steric effect. It is noteworthy that the nitration or bromination of acet-2-naphthalide proceeds to give substitution predominantly in the 1-position while no 1-substitution occurs in the Friedel-Crafts reaction with this compound or with the 2-bromo- and 2-chloronaphthalenes. However, acylation in the 1-position readily takes place with 2-methoxynaphthalene. A comparison of the relative size of these groups (7) shows that the methoxyl group is effectively smaller than the others.

Due to steric factors, the Friedel-Crafts acetylation of aminonaphthalenes cannot be considered as a means of preparing precursors in the synthesis of benzocinnolines.

In an attempt to prepare aminoacetonaphthones in which the amino and acetyl groups would occupy a vicinal position, 2-hydroxy-1-acetonaphthone and 1-hydroxy-2-acetonaphthone were subjected to a Bucherer type reaction with calcium chloride ammonia. In the former case, the acetyl group was cleaved from the ring and the resulting 2-naphthol either partially or completely converted to 2-naphthylamine. No definite products could be isolated in the case of 1-hydroxy-2-acetonaphthone.

BIBLIOGRAPHY

1. Borsche and Herbert, Ann., 546, 293 (1941).

2. Leonard and Boyd, J. Org. Chem., 11, 405 (1946).

3. Schofield and Simpson, J. Chem. Soc., 520 (1945).

4. Leonard and Boyd, J. Org. Chem., 11, 419 (1946).

5. Brown, Jacobs, Winstein, Levy, Moss and Ott, J. Org. Chem., 11, 163 (1946).

6. Dziewonski and Sternbach, Bull. intern. acad. polonaise, 59 (1931 A).

7. Adams and Yuan, Chem. Reviews, 12, 261 (1933).

VITA

The author was born near Stewartstown, Pennsylvania, on April 17, 1921. He attended the elementary school of Cross Roads Borough and was graduated from the Red Lion High School in June, 1938. In the fall of 1939, he entered the Pennsylvania State College and received the Bachelor of Science degree from that institution in December, 1942. In February of 1943, he entered the Graduate College of the University of Illinois from which he received the degree of Master of Science in Chemistry in 1944. In July, 1944, he entered the U. S. Navy. He was released to inactive duty with the rank of Lt. (j.g.), U.S.N.R. in October, 1946, and early in 1947 returned to the University of Illinois to complete his work for the doctorate. During the course of his graduate studies, he was employed as a part-time teaching assistant and held a University of Illinois Fellowship.

Digitized by the Internet Archive
in 2026

https://archive.org/details/IA41549807_0057